

*Received June 6, 2015; reviewed; accepted August 25, 2015*

## ACTIVATED LIGNIN AND AMINOSILANE-GRAFTED SILICA AS PRECURSORS IN HYBRID MATERIAL PRODUCTION

Lukasz KLAPISZEWSKI\*, Tadeusz Jan SZALATY, Jakub ZDARTA,  
Teofil JESIONOWSKI

Poznan University of Technology, Faculty of Chemical Technology, Institute of Chemical Technology and Engineering, Berdychowo 4, PL-60965, Poznan, Poland

\* e-mail: lukasz.klapiszewski@put.poznan.pl, phone: +48 616653747, fax: +48 616653649

**Abstract:** Functional inorganic-organic hybrids were synthesized using as a precursor silica with the addition of an appropriate amount of lignin as components. Three types of silica were applied as the support: the commercial silicas Syloid 244 and Aerosil 200, and hydrated silica precipitated in a polar system. The silicon dioxide was initially functionalized with aminosilane to activate the surface, and then the silica-based material was combined with lignin oxidized using hydrogen peroxide. The obtained inorganic-organic hybrids underwent physicochemical and dispersive-morphological analysis, with comparison of the results depending on the composition of the test samples. In addition, particle size distributions were determined and the surface structure of the products assessed by scanning electron microscopy. The presence of functional groups was also determined by FTIR spectroscopy. The thermal analysis of the silica/lignin materials was also performed, as well as the elemental and colorimetric analyses, which indirectly confirmed the correctness of the synthesis process. Hybrid materials with the most favorable dispersive and morphological properties were obtained by adding a small amount of biopolymer. The thermogravimetric analysis of the SiO<sub>2</sub>/lignin hybrids indicated their good thermal stability. With increasing quantity of lignin per 100 parts by weight of silica matrix, progressive deterioration in the thermal stability of the materials was observed.

**Keywords:** *SiO<sub>2</sub>/lignin hybrids, silica, lignin, lignin activation, thermal stability, hybrid material*

### Introduction

Silica/lignin hybrid materials are novel products with applications in many branches. The presence in the lignin molecule of many different functional groups containing oxygen enables the functionalization of its surface with SiO<sub>2</sub>. This process is accompanied by the creation of a greater number of active sites, which increase the capacity to adsorb hazardous metal ions, organic compounds and many harmful

substances (Hasegawa et al., 1999, Telysheva et al., 2009, Klapiszewski et al., 2015). The high adsorption capacity gives rise to prospective applications especially in protection of the environment. Silica/lignin materials can be used as promising advanced functional products, which are generally characterized as those materials which possess particular native properties and functions of their own (Klapiszewski et al., 2013a). The prevalence and natural character of lignin in combination with silica makes it an excellent filler for polymeric materials, which allows desired properties of the product to be obtained (Bula et al., 2015). Additionally, the composites can be used in electrochemistry, as modified electrodes, as well as for manufacture of electrochemical sensors and electroanalyzers (Lota and Milczarek, 2011, Jesionowski et al., 2014a, Jesionowski et al., 2014b). Moreover, this hybrid material can be used as a precursor of advanced composites, e.g. in preparation of silicon carbide of high purity, lignin/SiO<sub>2</sub>/TiO<sub>2</sub> and lignin/titania hybrids as precursors for Si–Ti–C–O fibers (Hasegawa et al., 1998, Hasegawa et al., 1999, Mishra et al., 2009).

Silica, in general, is an amorphous substance, with high chemical resistance, and therefore products of extremely high quality can be manufactured. A number of preparation techniques are used, which differ in terms of either the type of reagents or properties of the final product. Amongst many methods of silica preparation, the most commonly used are the flame process (Bergna and Roberts 2006, Wypych, 2010), hydrolysis and condensation of alkoxides developed by Stober (Stober et al., 1968), precipitation from aqueous sodium silicate solutions (Zurawska et al., 2003) and coprecipitation from emulsion systems (Jesionowski, 2001, Jesionowski, 2009). High demand for silica and its widespread use are linked to its valuable physicochemical properties and highly developed surface area. The fumed silica is made from primary particles with the spherical shape and size of approximately 20 nm, which form a chain structure of agglomerates. Generally, the surface has hydrophilic character due to the presence of silanol groups in the amount of 5–6 OH/nm<sup>2</sup>. It is a high activity product mainly used as a thixotropic agent, additive for paints and a material of toothpaste and pharmaceuticals. In turn, the precipitated silicas as well as silica gels have a much smaller degree of particle dispersion. The amount of silanol groups on nm<sup>2</sup> for precipitated silicas is about 15. They are commonly used as components of rubber compounds. In contrast, silica gels are materials mostly dedicated to adsorption processes or used as carriers. An additional advantage is the potential for surface functionalization to modify its chemical and physical character and extend the range of possible applications of synthetically obtained silicas (Krysztafkiewicz et al., 1997, Tertykh et al., 2003, Jesionowski et al., 2010, Tertykh et al., 2013).

Lignin is a naturally occurring aromatic cross-linked polymer made up of three main phenylpropane units, namely coniferyl, sinapyl and *p*-coumaryl alcohols (Donaldson, 2001, Meister, 2002, Ralph et al., 2004). The composition of each lignin monomer differs significantly depending on the type of plant material. Three types are commonly known: softwood (gymnosperm), hardwood (angiosperm), and grass or annual plant (graminaceous) lignin (Kadokawa, 2013).

In plants, lignin acts as a biological barrier and as a glue that binds hemicelluloses and celluloses in a cell wall. It is used as a composite filler, surfactant or dispersant additive, and as a component in binders and coatings. Lignin as a primary substance (wood) is insoluble in water, although it can be dissolved in acetone, pyridine and dimethyl sulfoxide (DMSO). It is easily decomposed in nature by the chemical action of enzymes. Lignin undergoes reactions of oxidation, reduction, bleaching and hydrolysis. The reactivity is due to its ability to form reactive intermediates derived from hydroxyl-phenyl groups (Boerjan, 2003, Vanholme, 2010). This complex compound can be selectively modified in an oxidative functionalization process due to the presence of a large number of side-chain aliphatic –OH groups, terminal phenolic groups and reactive benzylic positions (Crestini, 2010).

Over many years various chemical oxidants of lignin have been investigated. Strong oxidizing agents break up the aromatic ring, whereas milder ones cause changes only in the side chains. Oxidation has a significant influence on surface activation of lignin when hydroxyl groups are abundant. When these hydroxyl groups are oxidized, carbonyl groups are formed, which are more susceptible to reactions than hydroxyl groups. Moreover, this process improves the hydrophilicity of lignin (Kadokawa, 2013). Oxidative valorization of lignin can be performed in various ways.

Activated hydrogen peroxide oxidizes phenols or methoxybenzene to regioisomeric benzoquinones. Phenolic model compounds are converted into monoaromatic benzoic acid derivative, phenyl methyl ketone derivative, syringol and unsaturated lactone. Additionally, the ring cleavage reactions occur. Transformation of neolignans undergoing demethylation oxidation of the benzylic position, and the reaction where the ring is opened are also present. Oxidation of phenolic substrates requires extreme process conditions with an excess of toxic oxidant, but methyltrioxorhenium (MTO) is able to activate hydrogen peroxide under mild conditions (Lange, 2013).

Other compounds used to activate either molecular oxygen or hydrogen peroxide include salen complexes, especially cobalt with salen. During this oxidation process, from basic cinnamic ester and complex phenolic and non-phenolic phenylcoumaranes, there are obtained benzoquinone derivatives, alkyl-phenyl ketones, benzoic acid derivatives and benzofuran, respectively (Lange 2013).

Oxidation can be carried out in the presence of [Co(salen)] complexes with addition of ionic liquid. Various chemical oxidation reactions of lignin in ionic liquid have been investigated over many years. Scientists have used the fact that lignin is freely soluble in ionic liquids and catalytic oxidation of lignin has been carried out. Zakzeski et al. (2010, 2011) performed oxidation of lignin using 1-ethyl-3-methylimidazolium diethylphosphate ([Emim][DEP], cobalt catalyst and molecular oxygen under mild conditions.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in Emim DEP proved particularly effectiveness for oxidation. Based on ATR-IR spectroscopy it was shown that the catalyst oxidized benzyl and other alcohols rapidly occur in lignin, but they leave phenolic functionality and 5-5',  $\beta$ -O-4 and phenylcoumaran linkages intact (Zakzeski et al., 2010). The Co/[Emim][DEP] catalyst system represents a potential method in a

biorefinery scheme because it is able to increase the functionality of lignin (Zakzeski et al., 2011).

Oxidative valorization of lignin mainly proceeds in the presence of enzymes, such as laccases, lignin peroxidases (LP) and manganese dependent peroxidases (MnP). Synthetic metalloporphyrins are used as biomimetic systems for enzymes, like LP and MnP, and are oxidized with highly efficient metallo-oxo species similar to those in LP I and LP II. Highly functionalized porphyrins bearing aryl substituents in the meso-positions of the ring act as catalyst systems to oxidants, while careful modification of the nature of the meso-substituents can affect the redox potential and solubility of the complexes (Crestini, 1999).

Lignin can be effectively oxidized by porphyrin catalysts such as cationic manganese-meso-tetra(*N*-methylpyridinio)porphorin-pentaacetate  $TP_yMePMn(MeCOO)_5$ , which in this process leads to products such as benzoquinones, benzyl alcohols, and phenyl alkyl ketones in acidic environments (pH 3–6). All porphyrin catalysts such as anionic manganese and iron meso-tetra(2,6-dichloro-3-sulfonatophenyl) porphyrin chlorides (TDCSPPMnCl and TDCSPPFeCl), respectively, anionic meso-tetra-4-sulfonatophenyl porphyrin chloride (TSPPMnCl), and the previously mentioned cationic manganese meso-tetra(*N*-methylpyridinio)-porphorin-pentaacetate ( $TP_yMePMn(MeCOO)_5$ ), despite the different metal centers and porphyrin moieties, undergo comparable reaction mechanisms and produce comparable products (Lange, 2013).

In this paper a trial was undertaken to synthesize and characterize silica/lignin hybrid materials. For the first time, hydrogen peroxide was used to oxidize the appropriate functional groups in lignin and increase the affinity of the biopolymer to the aminosilane-grafted silica. The effectiveness of combination of silica with lignin was confirmed by the FTIR spectroscopy and elemental analysis, and also indirectly by the colorimetric analysis. The hybrid systems were examined by determining their dispersive (NIBS technique), morphological (SEM images) and thermal (TGA analysis) properties. In the near future, these studies will lead to the potential use of these systems in a variety of applications.

## Experimental

### Preparation of hydrated silica in a polar medium

The product was synthesized by means of a reaction of aqueous solution of sodium silicate (Vitrosilicon S.A., Poland) with 5 % sulfuric acid (Chempur, Poland) (Fig. 1). A reactor containing 100 cm<sup>3</sup> of aqueous solution of hydrophobizing agent (0.2 g Rokanol K7 – PCC Rokita, Poland), was placed into a water bath (85 °C). To this system 9.8 g sodium sulfate (Chempur, Poland) was added. In the next step, the sodium silicate solution at a constant rate of 8 cm<sup>3</sup>/min, and 5 % solution of sulfuric acid at the desired rate of 4 cm<sup>3</sup>/min were added. The system was intensively stirred and the process was conducted for about 1 h. The obtained silica was filtered by suction and washed several times with water. A white precipitate was placed in a

crystallizer and subjected to convective drying at 105 °C for about 24 h. More details are given in our previously published work (Klapiszewski et al., 2012).

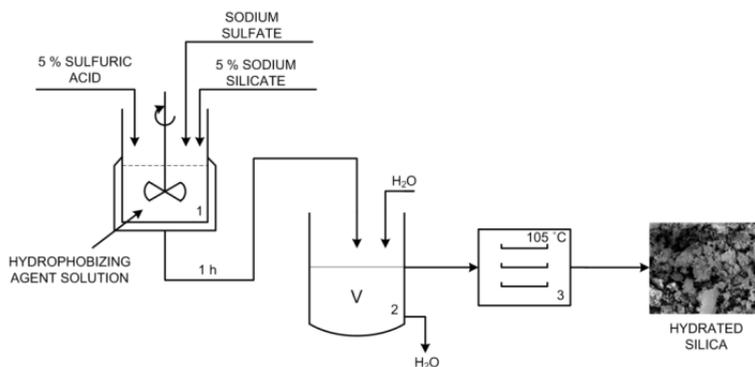


Fig. 1. Technological process for production of silica in a polar medium (1 – mixing device, 2 – vacuum filter, 3 – convection dryer)

### Functionalization of silica surface using aminosilane

In this study, the commercial silicas Aerosil 200 (Evonik Industries AG, Germany) and Syloid 244 (W.R. Grace Co., USA) were used. The three types of tested silicas (Aerosil 200, Syloid 244 and hydrated  $\text{SiO}_2$ ) were subjected to grafting with a water/methanol solution (1:4, v/v) containing *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (in a quantity of 5 parts by weight per 100 parts of  $\text{SiO}_2$ ). The solution was applied on the surface of the silica using an atomizer, mixing thoroughly after each application. The modified silica was dried for 24 h at 105 °C (see Figure 2). A precise description of modification is contained in our previous publications (Jesionowski and Krysztafkiwicz, 2000; Jesionowski et al., 2010).

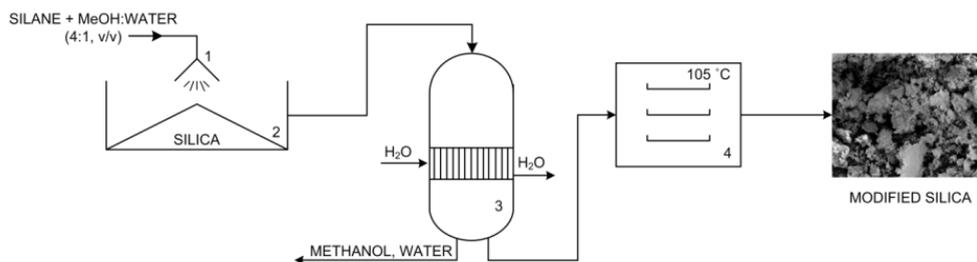


Fig. 2. Functionalization of silica surface by aminosilane (1 – atomizer, 2 – reactor, 3 – vacuum evaporator, 4 – convection dryer)

### Preparation of silica/lignin hybrids using lignin oxidized by $\text{H}_2\text{O}_2$

The first step in modification of silica with kraft lignin (L) was preparation of 7.5 % solution of hydrogen peroxide, into which an appropriate amount of lignin was

introduced. Kraft lignin was purchased from Sigma-Aldrich (Germany). The BET surface area of lignin was  $1 \text{ m}^2/\text{g}$ , while the pore size was equal to 12.1 nm. Lignin had a particle size in the range of 1990-2670 and 3580-5560 nm. The process of activation of lignin was carried out without light. The solution of lignin prepared in this way was stirred for about 20 min. In the second step, aminosilane-modified silica (Aerosil 200 (A), Syloid 244 (S) or hydrated silica (H)) was added to the prepared reaction mixture, and then the reacting system was constantly stirred for 1 h. The obtained product (silica/lignin hybrid material) was placed in a convective dryer to evaporate water and dried overnight at  $50 \text{ }^\circ\text{C}$ . The amounts of the precursors used for silica/lignin samples obtained are summarized in Table 1.

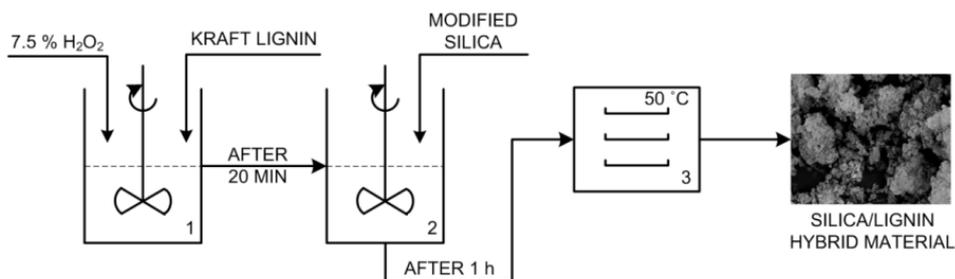


Fig. 3. Technological process for production of silica/lignin hybrid material (1, 2 – reactor, 3 – convection dryer)

Table 1. The amounts of precursors used to obtain a silica/lignin hybrid materials

| Sample             | Content of lignin in relation to the modified silica matrix (wt./wt.) | Amount of kraft lignin (g) | Amount of silica (Syloid 244 / Aerosil 200 / hydrated silica) (g) |
|--------------------|---|----------------------------|---|
| SL 1 / AL 1 / HL 1 | 3   | 0.15                       |   |
| SL 2 / AL 2 / HL 2 | 10  | 0.5                        |   |
| SL 3 / AL 3 / HL 3 | 20  | 1.0                        | 5.0   |
| SL 4 / AL 4 / HL 4 | 50  | 2.5                        |   |

### Evaluation of physicochemical properties

The dispersive and morphological properties of the silica/lignin hybrid materials were characterized by particle size determination using a Zetasizer Nano ZS (0.6–6000 nm) instrument (Malvern Instruments Ltd., UK), operating based on the non-invasive backscattering (NIBS) technique. To obtain information on dispersion, particle morphology and type of agglomeration in the samples as well as images from a scanning electron microscope (Zeiss EVO40, Germany) were used. Prior to tests, the samples were coated with Au for 5 seconds using a Balzers PV205P coater.

The elemental contents of the products were established with the use of a Vario EL Cube instrument made by Elementar Analysensysteme GmbH (Germany), which is capable of registering the percentage content of carbon, hydrogen, nitrogen and sulfur in samples after high-temperature combustion. The results are obtained by averaging three measurements with an error of  $\pm 0.01$  %.

Fourier transform infrared spectroscopy (FTIR), using a Vertex 70 spectrometer (Bruker, Germany), was used to prove the presence of expected functional groups. The materials were analyzed in the form of tablets, made by pressing a mixture of anhydrous KBr (ca. 0.1 g) and 1 mg of the tested substance in a special steel ring under a pressure of approximately 10 MPa. The tests were performed over a wavenumber range of 4000–400  $\text{cm}^{-1}$  (at a resolution of 0.5  $\text{cm}^{-1}$ ).

A thermogravimetric analyzer (TGA, model Jupiter STA 449F3, made by Netzsch, Germany) was used to investigate the thermal stability of the samples. The measurements were carried out under liquid nitrogen (10  $\text{cm}^3/\text{min}$ ) at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  over a temperature range of 25–1000  $^{\circ}\text{C}$ , with an initial sample weight of approximately 5 mg.

Colorimetric characterization of the silica/lignin hybrid materials was carried out by using a Specbos 4000 colorimeter (YETI Technische Instrumente GmbH, Germany). The results are given in the *CIE Lab* system, where  $L^*$  denotes lightness;  $+a^*$ ,  $-a^*$ ,  $+b^*$ ,  $-b^*$  contribution of red, green, yellow and blue, respectively. The total change in color is denoted by  $dE$ .

## Results and discussion

### Dispersive-morphological properties

Synthesis of silica/lignin hybrids was carried out using three types of silica (Syloid 244, Aerosil 200, and specially prepared hydrated silica), the surface of which was initially modified by aminosilane. Each of the three types of silica (Table 2), the presence of single primary particles of nanometric size, which tend to create aggregates ( $<1$   $\mu\text{m}$ ), as well as agglomerates ( $>1$   $\mu\text{m}$ ), can be noticed. In the process of hybrid material synthesis, a constant quantity of silica was used, with the addition of appropriate quantities of lignin and  $\text{H}_2\text{O}_2$  oxidant. The SEM images of silicas and kraft lignin used have already been presented in our previous publications (Klapiszewski et al., 2013b, Klapiszewski et al., 2014, Jesionowski et al., 2014b).

The particle size distributions obtained for the silica/lignin hybrid materials are nano- and micrometric (Table 2). The primary particles in sample SL 1 have sizes in the range of 79–142 nm, and comparable results were recorded for samples SL 2 and SL 3. Slightly higher particle sizes equal to 142–220 nm were obtained with the hybrid material containing the largest quantity of lignin (50 parts by weight). These particles showed a tendency to form agglomerates. It was shown that the higher the quantity of lignin in the material, the greater is this tendency. The size of the agglomerates is 1480–4150 nm in the first sample, and 1480–5560 nm in the last one.

Table 2. Particle size distribution for precursors and for obtained silica/lignin hybrid materials

| Sample                        | Type of silica  | Content of lignin in relation to the modified silica matrix (wt./wt.) | Particle size distribution (Zetasizer Nano ZS) (nm) |
|-------------------------------|-----------------|---|---|
| Syloid 244                    | Syloid 244      |   | 39-68; 1720-2300                                    |
| Syloid 244 + aminosilane      |                 |   | 51-79; 1720-2670                                    |
| Aerosil 200                   | Aerosil 200     |   | 68-106; 1480-3370                                   |
| Aerosil 200 + aminosilane     |                 |   | -   |
| Hydrated silica               | Hydrated silica |   | 44-59; 1110-5560                                    |
| Hydrated silica + aminosilane |                 |   | 59-106; 1480-5560                                   |
| Lignin                        | -               |   | 1990-2670; 3580-5560                                |
| SL 1                          | Syloid 244      | 3   | 79-142; 1480 4150                                   |
| SL 2                          |                 | 10  | 91-122; 1280-4800                                   |
| SL 3                          |                 | 20  | 91-142; 1280-5560                                   |
| SL 4                          |                 | 50  | 142-220; 1480-5560                                  |
| AL 1                          | Aerosil 200     | 3   | 79-106; 1110-4800                                   |
| AL 2                          |                 | 10  | 106-142; 1280-5560                                  |
| AL 3                          |                 | 20  | 91-220; 2300-5560                                   |
| AL 4                          |                 | 50  | 122-295; 1720-5560                                  |
| HL 1                          | Hydrated silica | 3   | 79-220; 1990-5560                                   |
| HL 2                          |                 | 10  | 91-295; 2300-5560                                   |
| HL 3                          |                 | 20  | 91-342; 2670-5560                                   |
| HL 4                          |                 | 50  | 106-342; 2670-5560                                  |

The analysis using a Zetasizer Nano ZS apparatus, as well as the SEM images (Fig. 4), confirm a tendency of particles to form agglomerative systems. Particles of the composites exhibit irregular shapes.

In the further study, hybrid samples were prepared from a different commercial silica Aerosil 200, for which SEM images are shown in Fig. 5. The particle sizes, which were obtained, are relatively higher than those for the samples based on the previous silica, particularly in the case of the composite containing the greatest amount of lignin. The particles of this product show a tendency to form the agglomerates of size 1720–5560 nm and a slightly greater. This tendency is exhibited in this case by the hybrid material containing 20 parts by weight of lignin. The best dispersive-morphological properties were recorded for the material containing 3 parts by weight of lignin per 100 parts silica. The diameters are in the range 79–106 nm, with a tendency towards agglomeration in the range of 1110–4800 nm (Table 2).

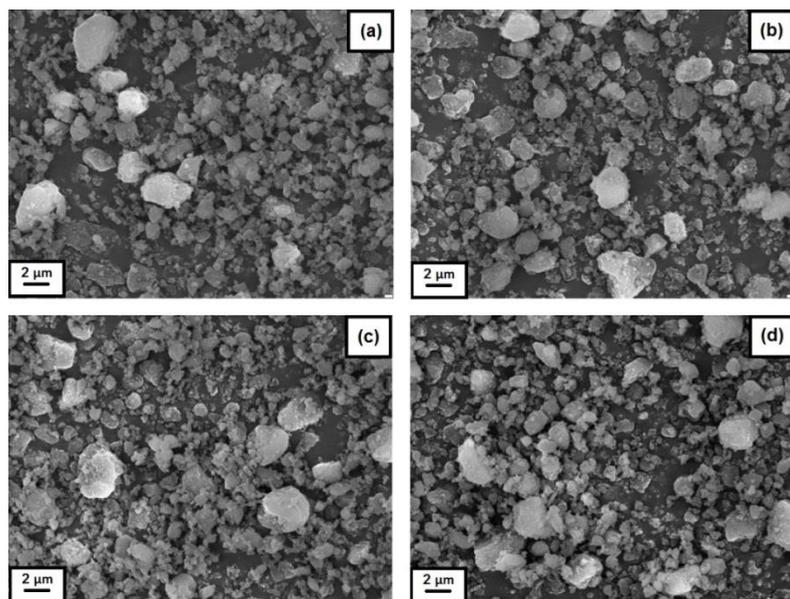


Fig. 4. SEM images of the silica/lignin hybrid materials labeled as (a) SL 1, (b) SL 2, (c) SL 3 and (d) SL 4

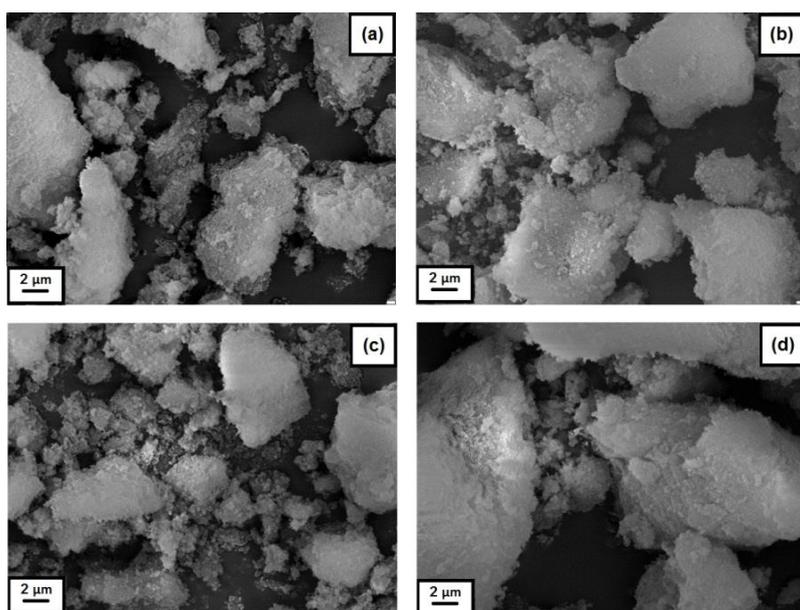


Fig. 5. SEM images of the silica/lignin hybrid materials labeled as (a) AL 1, (b) AL 2, (c) AL 3 and (d) AL 4

The SEM images (Fig. 5) indicate the presence of particles with irregular shapes. In addition, the presence of primary particles and a large number of secondary agglomerates was confirmed. As the quantity of lignin relative to the silica matrix increases, the individual molecules show a greater tendency to form the agglomerates.

Table 2 shows results of the dispersive properties of hybrids based on hydrated silica, recorded on a Zetasizer Nano ZS. The data show the products to have greater heterogeneity than the previously analyzed samples based on commercial silica. This finding is confirmed by the wide range of particle size distribution. A range of 79–220 nm was recorded for HL 1, rising with increasing quantity of biopolymer in the sample, up to 106–342 nm for the sample HL 4. With increasing content of lignin, the hybrid samples show an increasing tendency towards agglomeration, similarly to the previous samples. The particles based on hydrated silica show a markedly greater tendency to form agglomerates, but in each of these products the agglomerates reach a size of 5560 nm. The results are confirmed by the SEM images (Fig. 6) showing the presence of small particle agglomerates and larger clusters. The SEM images indicate the presence of particles of irregular shapes.

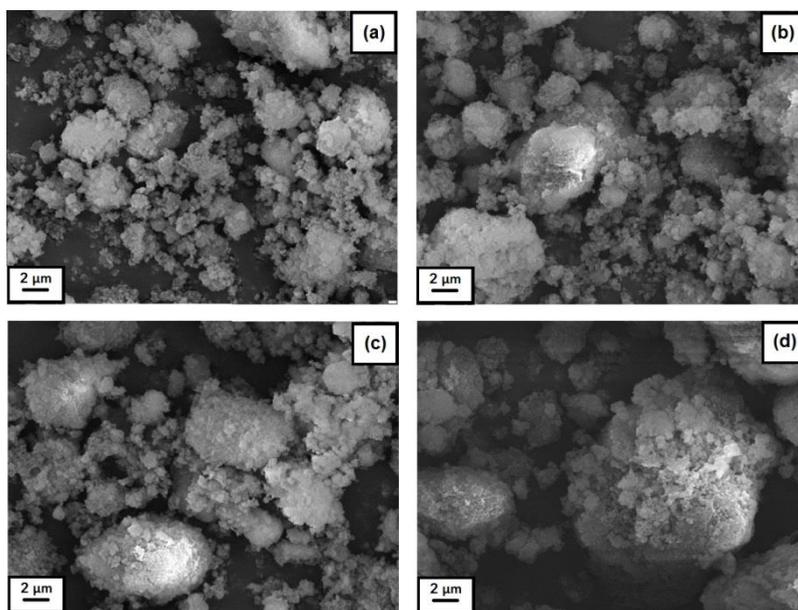


Fig. 6. SEM images of silica/lignin hybrids based on hydrated silica: (a) HL 1, (b) HL 2, (c) HL 3 and (d) HL 4

The pure silicas have nanometric particles with tendency to aggregation and agglomeration. A small addition of lignin in silica/lignin hybrids already causes a slight increase in the particle size. Moreover, with increasing content of lignin the amount of agglomerates increases, as shown by the data from Zetasizer Nano ZS (Table 2) and SEM images (Figs. 4-6). It should be mentioned that the commercial

kraft lignin used in the study contains the particles of sizes representing a wide range, what indicates the possibility of large agglomerates formation.

### **Elemental analysis**

Based on the results of elemental analysis, the contents of nitrogen, carbon, hydrogen and sulfur in the analyzed samples were determined. The results given in Table 3, indirectly confirm the effectiveness of the methodology for silica/lignin hybrid synthesis. The results show that after modification of silica using aminosilane the content of nitrogen increased to 0.52% for Syloid 244, 0.54% for Aerosil 200) and 0.55% for hydrated silica). It indicates on indirect evidence of the presence of this element in the used silane. Lignin contains in its structure approximately 3 % by mass of sulfur, derived from the kraft process. The increase in the quantity of this element with increasing lignin content in the hybrid materials serves as evidence of successful interconnection of the biopolymer with the modified silica surface. The analyzed samples were found to contain quantities of nitrogen, which comes from the silica modifier. In comparison to the aminosilane-grafted silica samples the percentage content of nitrogen for silica/lignin hybrid materials slightly decreased. As the weight contribution of lignin in proportion to silica increases, an increase in carbon and hydrogen content being the main building elements of the biopolymer structure was observed. The results given in Table 2 support the conclusion that, based on all of the silicas used, expected and desirable hybrid systems were obtained. Hydrated silica appears to be the best support, since it shows the highest increase in the content of individual elements as the lignin contribution rises. For a sample containing 50 parts by weight of kraft lignin per 100 parts of hydrated silica, a carbon contribution of 10.98% was recorded, which is greater than the value for product HL 1 (C = 3.01%). Moreover, attention should be paid to the results of the elemental analysis of pure silicas. In this case, there is a clear similarity in the results for the carbon and hydrogen contents. The low content of these elements indicates the high purity of silicas used in the research. The results of this analysis indirectly confirm the effective interconnection of each type of silica with kraft lignin, which supports the correctness of the methodology used in the experiments.

### **FTIR spectroscopy**

The FTIR analysis was performed to identify the functional groups present in the structure of silica, lignin and selected SiO<sub>2</sub>/lignin hybrid materials. The measurements were performed for samples of silica/lignin hybrids containing 3, 10, 20 and 50 parts by weight of lignin per 100 parts SiO<sub>2</sub>, obtained using commercial silicas and hydrated silica with the addition of lignin oxidized with H<sub>2</sub>O<sub>2</sub>.

Table 3. Elemental content of nitrogen, carbon, hydrogen and sulfur in precursors and silica/lignin hybrids

| Sample                        | Elemental content (%) |       |      |      |
|-------------------------------|-----------------------|-------|------|------|
|                               | N                     | C     | H    | S    |
| Syloid 244                    | –                     | 0.19  | 0.13 | –    |
| Syloid 244 + aminosilane      | 0.52                  | 1.32  | 1.42 | –    |
| Aerosil 200                   | –                     | 0.11  | 0.12 | –    |
| Aerosil 200 + aminosilane     | 0.54                  | 1.23  | 1.29 | –    |
| Hydrated silica               | –                     | 0.19  | 0.10 | –    |
| Hydrated silica + aminosilane | 0.55                  | 1.37  | 1.61 | –    |
| Lignin                        | –                     | 42.2  | 5.02 | 3.14 |
| SL 1                          | 0.32                  | 2.31  | 1.23 | 0.12 |
| SL 2                          | 0.30                  | 4.32  | 1.30 | 0.28 |
| SL 3                          | 0.26                  | 5.81  | 1.33 | 0.53 |
| SL 4                          | 0.21                  | 9.83  | 1.40 | 0.81 |
| AL 1                          | 0.35                  | 2.53  | 1.31 | 0.14 |
| AL 2                          | 0.33                  | 5.01  | 1.38 | 0.31 |
| AL 3                          | 0.29                  | 6.63  | 1.40 | 0.56 |
| AL 4                          | 0.27                  | 10.03 | 1.49 | 0.93 |
| HL 1                          | 0.36                  | 3.01  | 1.34 | 0.16 |
| HL 2                          | 0.33                  | 5.89  | 1.45 | 0.38 |
| HL 3                          | 0.30                  | 7.05  | 1.49 | 0.71 |
| HL 4                          | 0.28                  | 10.98 | 1.56 | 1.08 |

The spectra of the pure silicas (Fig. 7a shows a single common spectrum for Aerosil and Syloid silicas because of their very great similarity) reveal the presence of physically bound water, as confirmed by the broad band in the range 3600–3200  $\text{cm}^{-1}$  coming from stretching vibrations of O–H groups. Additionally, a band at wavenumber 1650  $\text{cm}^{-1}$  is caused by bending vibrations of the same group. The bands that occur at 1200–1000 and 810  $\text{cm}^{-1}$  are attributed to stretching vibrations of Si–O–Si. Stretching vibrations of Si–OH give rise to bands at wavenumber 960  $\text{cm}^{-1}$ , while the bands at 490  $\text{cm}^{-1}$  are attributed to stretching vibrations of Si–O. The results are consistent with data presented elsewhere (Roy et al., 2010, Klapiszewski et al., 2013b, Szwarc-Rzepka et al., 2013).

The FTIR spectrum of kraft lignin is presented in Fig. 7a. The results show the presence of stretching vibrations of O–H groups in the range 3600–3200  $\text{cm}^{-1}$ , and stretching vibrations of C–H ( $-\text{CH}_2$ ,  $-\text{CH}_3$ ) at 2950–2820  $\text{cm}^{-1}$ . Stretching vibrations from the ketone group C=O produce the bands at 1710–1550  $\text{cm}^{-1}$ , while those at 1600, 1510 and 1420  $\text{cm}^{-1}$  are attributed to stretching vibrations of the C–C, C=C bonds in the aromatic skeleton. Stretching vibrations of ether groups (C–O–C) appear at 1100–1000  $\text{cm}^{-1}$ , and other bands in the range 1360–1200  $\text{cm}^{-1}$  correspond to stretching vibrations of C–O (C–O(H), C–O(Ar)). Below 1000  $\text{cm}^{-1}$  the spectrum contains bands attributed to in-plane and out-of-plane vibrations of aromatic C–H bonds. The presented analysis of kraft lignin is in agreement with previously published data (Klapiszewski et al., 2013b; Tejado et al., 2007).

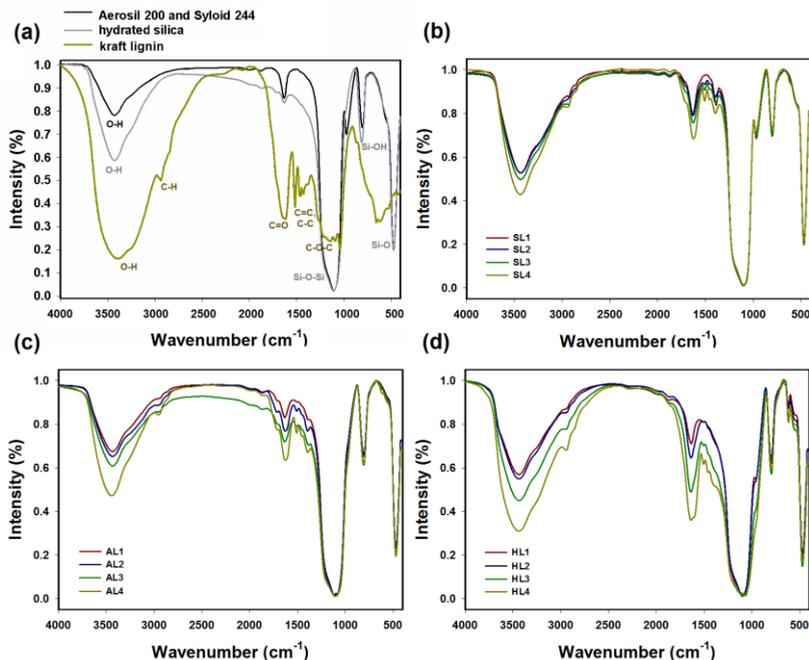


Fig. 7. FTIR spectra of precursors (a) and silica/lignin hybrids based on Syloid 244 (b), Aerosil 200 (c) and hydrated silica (d)

Selected  $\text{SiO}_2$ /lignin hybrids were also analyzed. The analyzed samples contain 3, 10, 20 and 50 parts by weight of lignin oxidized by hydrogen peroxide per 100 parts  $\text{SiO}_2$ . Based on the FTIR spectra (see Figs. 7b-d), the presence of characteristic functional groups was verified. The spectra reveal the presence of the characteristic bonds coming from silica: Si–O–Si symmetric stretching vibrations at 1200–1050  $\text{cm}^{-1}$  and asymmetric stretching vibrations at 800  $\text{cm}^{-1}$ . The bands at 960  $\text{cm}^{-1}$  are attributed to stretching vibrations of Si–OH, and bending vibrations of Si–O appear at 485  $\text{cm}^{-1}$ . An important broad band in the range of 3600–3200  $\text{cm}^{-1}$  comes from stretching vibrations of O–H groups, which occur in the structure of both lignin and silica. Moreover the functional groups observed in pure lignin are present: C–H bonds at 3000–2800  $\text{cm}^{-1}$  and different types of carbon atom bonds in the range of 1650–1300  $\text{cm}^{-1}$ . The number of C=O, O–C–O and O=C–O bonds was greater than in kraft lignin.

The FTIR spectra presented in Figs. 7b and 7c belong to hybrids based on the commercial silicas Syloid 244 and Aerosil 200 respectively. Based on the FTIR spectra for the pure precursors and for the materials obtained, it is observed that the intensity of bands was greater in the hybrids than in the pure materials. This confirms the effectiveness of the proposed method of synthesis, which is associated with an increase in the intensity of the bands corresponding to the relevant functional groups. Furthermore, the intensity of bands increases with increasing the content of lignin in

the hybrid material, and larger intensities were observed with the use of hydrated silica (Fig. 7d). The proposed mechanisms for combination of silica with lignin (a biopolymer activated using sodium periodate) were described by Jesionowski et al. (2014 b).

### TGA analysis

Thermal stability measurements of silica, lignin and inorganic-organic materials were performed. The resulting thermogravimetric curves show the mass loss of samples caused by the transitions that occur as the temperature increases.

Figure 8a shows the TGA curves obtained for the precursors used. Syloid 244 silica shows high thermal stability. A mass loss was observed at 100 °C (of about 5 %; all types of silica gave similar TGA curves, so only the curve for Syloid 244 is shown), associated with the loss of water structurally bound with the precursor. In the case of lignin the thermogravimetric curve shows a clearly larger mass loss in comparison with silica. The TGA curve recorded for lignin indicates a significant mass loss of about 65 % relative to the initial mass of the sample. The first small mass loss of about 10 % taking place at 20–150 °C is mainly a result of the removal of water bound to the lignin surface. The second, larger mass loss of about 35 % taking place in the range 200–600 °C is related to the complex thermal decomposition of lignin, involving the formation of new bonds as a consequence of crosslinking reactions. The third mass loss of about 15 % observed in the range 600–1000 °C is interpreted as a consequence of the partial elimination of carbon fragments caused by fragmentation of the molecules in uncontrolled and undetermined reactions.

Figure 8b shows the thermogravimetric curves of silica/lignin hybrids based on Syloid 244. Sample SL 4, which has the highest content of lignin in proportion to silica among the analyzed products, showed the lowest thermal stability. An increasing content of lignin in the product causes a decrease in thermal stability, as indicated by the larger mass loss. The shape of the TGA curves is similar to that obtained for pure lignin; in the case of the materials there are again present three visible stages, the most visible in the sample with 50 parts by weight of lignin. The product containing 3 parts of lignin exhibits the smallest mass loss.

Additional confirmation of the decreasing thermal stability with increasing lignin content is provided by the TGA curves for hybrids based on Aerosil 200 (Fig. 8c). These results show that composites based on this silica have the best thermal stability when the lignin content is the smallest.

Hybrids based on hydrated silica (Fig. 8d) exhibit poorer thermal stability than samples containing the commercial silicas Syloid 244 and Aerosil 200 (Figs. 8b and 8c). A common feature is that the mass loss is larger with an increase in lignin content in every case. In this case, however, mass loss is observed at lower temperatures than with the previous samples.

The final hybrid materials show rather greater thermal stability than is exhibited by pure lignin. In summary, the thermal analysis showed that the higher the content of

lignin in the product, the poorer its thermal stability. Moreover, with an increase in lignin content, the TGA curves become more similar to those of pure lignin, and the mass loss is larger. This may be caused by either a lack of oxidation or degradation of the materials. As regards the type of silica used, the best properties are exhibited by the commercial silica Aerosil 200, and the worst by hydrated silica. These results may indicate that the synthesis of lignin with hydrated silica is less effective in hybrid formation than the method using commercial silica. The attractive TGA results obtained at this stage of the study suggest that the silica/lignin products can be used as a new generation of polymer fillers.

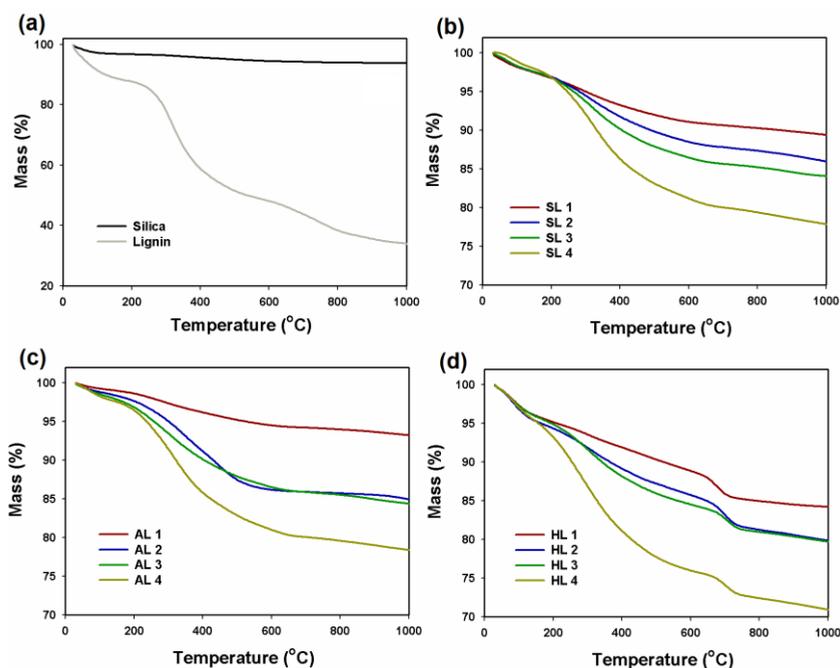


Fig. 8. Thermal stability of silica and lignin (a) and silica/lignin hybrids based on Syloid 244 (b), Aerosil 200 (c) and hydrated silica (d)

### Colorimetric analysis

For the synthesized silica/lignin products as well as for the initial precursors, the colorimetric analysis was carried out using the  $CIE L^*a^*b^*$  color system. The results obtained for the pure precursors are given in Table 4. Silica is white, while lignin is a dark-brown solid. The parameter  $L^*$ , which determines lightness, shows that the highest lightness is provided by the commercial silica Aerosil 200 (93.78), a very similar value is recorded for Syloid 244, and slightly worse results are obtained in the case of hydrated silica (92.93). Because of its dark color, the lightness value of lignin is 41.26. In the case of the parameters  $a^*$  and  $b^*$ , reflecting the contribution of red and

yellow color in the sample, the lowest values are obtained for the hydrated silica, with increased values for the commercial silicas, while for pure lignin the values are 10.16 ( $a^*$ ) and 25.92 ( $b^*$ ). Another important parameter in the colorimetric analysis is the  $dE$  variable, which determines the total color change.

Table 4. Colorimetric data for silicas, lignin and SiO<sub>2</sub>/lignin products

| Sample                        | Colorimetric data |       |       |       |
|-------------------------------|-------------------|-------|-------|-------|
|                               | $L^*$             | $a^*$ | $b^*$ | $dE$  |
| Syloid 244                    | 93.63             | 0.22  | 2.13  | -     |
| Syloid 244 + aminosilane      | 93.58             | 0.22  | 2.15  | -     |
| Aerosil 200                   | 93.78             | 0.24  | 2.55  | -     |
| Aerosil 200 + aminosilane     | 93.72             | 0.23  | 2.54  | -     |
| Hydrated silica               | 92.93             | 0.18  | 2.01  | -     |
| Hydrated silica + aminosilane | 92.90             | 0.19  | 1.97  | -     |
| Lignin                        | 41.26             | 10.16 | 25.92 | -     |
| SL 1                          | 88.91             | 3.56  | 10.31 | 13.85 |
| SL 2                          | 82.35             | 3.98  | 12.37 | 15.91 |
| SL 3                          | 75.34             | 4.53  | 13.77 | 19.43 |
| SL 4                          | 71.15             | 5.53  | 15.01 | 21.98 |
| AL 1                          | 87.35             | 3.05  | 9.89  | 13.15 |
| AL 2                          | 81.19             | 4.18  | 11.93 | 16.03 |
| AL 3                          | 77.03             | 4.87  | 14.87 | 17.93 |
| AL 4                          | 72.83             | 6.13  | 15.93 | 22.19 |
| HL 1                          | 86.05             | 2.95  | 9.93  | 13.98 |
| HL 2                          | 80.15             | 4.03  | 12.33 | 15.32 |
| HL 3                          | 75.98             | 4.78  | 16.66 | 19.97 |
| HL 4                          | 70.01             | 6.90  | 17.17 | 24.88 |

Table 4 contains data obtained from the colorimetric analysis of silica/lignin materials. The samples were prepared by addition of different quantities of lignin oxidized by H<sub>2</sub>O<sub>2</sub> to the selected type of silica. Modification of silica with aminosilane had no effect on lightness of the unmodified SiO<sub>2</sub> sample. Surface functionalization of silica using an appropriate amount of lignin solution caused a significant decrease in the lightness parameter  $L^*$ . For example, the reference sample (unmodified Syloid 244) had a value of  $L^*=93.63$ . Modification by different quantities of lignin caused a decrease in the parameter to  $L^*=88.91$  for sample SL 1 and to  $L^*=71.15$  for SL 4. A decrease in these values was also observed in the case of other samples, regardless of the type of silica.

The parameters  $a^*$  and  $b^*$  reflect the change in the contribution of the colors red and yellow, respectively, as a result of modification of silica by kraft lignin. The

colorimetric analysis shows an increase in the contribution of red color with an increase in the lignin content of the sample. The change in the contribution of yellow is not so significant, but also shows a slight upward trend. This can be seen in the color of the obtained biomaterials – from light beige to dark brown. The  $dE$  parameter was used to describe the complete change of color. This also confirms the correctness of the measurements performed, as the value initially increases with increasing content of lignin in the product. The greatest differences can be seen between the samples containing 3 and 50 parts by weight of lignin per 100 parts silica, for which the respective values of  $dE$  are 13.98 (HL 1) and 24.88 (HL 4).

The colorimetric analysis showed that a small addition of lignin causes a significant change in all of the listed parameters describing the color space  $CIE L^*a^*b^*$ , with respect to the initial silica used as the point of reference. Lower values of the lightness  $L^*$ , and higher values of the parameters  $a^*$  and  $b^*$ , were recorded for the hybrids based on hydrated silica in comparison with those based on commercial silicas. These changes are conditioned by, among other things, the types of  $SiO_2$  used, as shown by the data in Table 4.

## Conclusions

The proposed method of preparation of silica/lignin hybrids, based on silica surface-functionalized with  $H_2O_2$  oxidized lignin solution, makes it possible to obtain a product with defined physicochemical and dispersive-morphological properties.

The particle size distributions and SEM images of silica/lignin hybrids indicate that an increase in the proportion of lignin in the material reduces the quantity of individual primary particles of small size, at the expense of the formation of larger groups of units. Products with the most favorable dispersive-morphological properties were obtained by adding a small amount of lignin.

The effectiveness of preparation of silica/lignin materials was confirmed by FTIR spectra. This analysis shows that the process for the preparation of the materials proceeded correctly. With an increase in the quantity of lignin used, better combination with the silica matrix was observed. The efficiency of precursors combination was also confirmed by the elemental analysis.

The thermogravimetric analysis of products indicates their good thermal stability in comparison with pure lignin. With an increasing quantity of lignin per 100 parts by weight of silica matrix, a progressive decline in the thermal stability of the materials was observed. The results obtained from the thermal analysis indicate that the hybrids created based on silica and lignin will successfully find application as novel polymer fillers.

The colorimetric analysis showed that a small addition of lignin significantly alters the color parameters in the colorimetric system  $CIE L^*a^*b^*$  with respect to the initial silica used as the reference point. Moreover, values of parameter  $L^*$  indicated a decrease in lightness with increasing quantity of lignin in the material. An increase in

the lignin content of the hybrid materials also led to an increase in contribution of red color (parameter  $a^*$ ).

## Acknowledgements

The study was financed within the National Science Centre Poland funds according to decision no. DEC-2013/09/B/ST8/00159.

## References

- BERGNA H.E., ROBERTS W.O., 2006, *Colloidal Silica: Fundamentals and Applications*, Taylor & Francis Group, Boca Raton.
- BOERJAN W., RALPH J., BAUCHER M., 2003, *Lignin biosynthesis*. Annual Review of Plant Biology, 54, 519–546.
- BULA K., KLAPISZEWSKI L., JESIONOWSKI T., 2015, *A novel functional silica/lignin hybrid material as a potential bio-based polypropylene filler*. Polymer Composites, 36, 913–922.
- CRESTINI C., SALADINO R., TAGLIATESTA P., BOSCHI T., 1999, *Biomimetic degradation of lignin and lignin model compounds by synthetic anionic and cationic water soluble manganese and iron porphyrins*. Bioorganic & Medicinal Chemistry, 7, 1897–1905.
- CRESTINI C., CRUCIANELLI M., ORLANDI M., SALADINO R., 2010, *Oxidative strategies in lignin chemistry: A new environmental friendly approach for the functionalization of lignin and lignocellulosic fibers*. Catalysis Today, 156, 8–22.
- DONALDSON L.A., 2001, *Lignification and lignin topochemistry – an ultrastructural view*. Phytochemistry, 57, 859–873.
- HASEGAWA I., FUKUDA Y., OKADA T., KAJIWARA M., 1998, *Lignin-silica-titania hybrids as precursors for Si–Ti–C–O fibers*. Journal of Sol-Gel Science and Technology, 13, 485–488.
- HASEGAWA I., FUJII Y.S., YAMADA K., KARIYA C., TAKAYAMA T., 1999, *Lignin–silica hybrids as precursors for silicon carbide*. Journal of Applied Polymer Science, 73, 1321–1328.
- JESIONOWSKI T., KRYSZTAFKIEWICZ A., 2000, *Comparison of the techniques used to modify amorphous hydrated silica*. Journal of Non-Crystalline Solids, 277, 45–57.
- JESIONOWSKI T., 2001, *Preparation of colloidal silica from sodium metasilicate solution and sulphuric acid in emulsion medium*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 190, 153–165.
- JESIONOWSKI T., 2009, *Preparation of spherical silica in emulsion systems using the co-precipitation technique*. Materials Chemistry and Physics, 113, 839–849.
- JESIONOWSKI T., CIESIELCZYK F., KRYSZTAFKIEWICZ A., 2010, *Influence of selected alkoxyxilanes on dispersive properties and surface chemistry of spherical silica precipitated in emulsion media*. Materials Chemistry and Physics, 119, 65–74.
- JESIONOWSKI T., KLAPISZEWSKI L., MILCZAREK G., 2014a, *Structural and electrochemical properties of multifunctional silica/lignin materials*. Materials Chemistry and Physics, 147, 1049–1057.
- JESIONOWSKI T., KLAPISZEWSKI L., MILCZAREK G., 2014b, *Kraft lignin and silica as precursors of advanced composite materials and electroactive blends*. Journal of Materials Science, 49, 1376–1385.
- KADOKAWA J., 2013, *Applications of Ionic Liquids in Lignin Chemistry*, InTech, Rijeka.

- KLAPISZEWSKI L., MADRAWSKA M., JESIONOWSKI T., 2012, *Preparation and characterisation of hydrated silica/lignin biocomposites*. Physicochemical Problems of Mineral Processing, 48, 463–473.
- KLAPISZEWSKI L., NOWACKA M., SZWARC-RZEPKA K., JESIONOWSKI T., 2013a, *Advanced biocomposites based on silica and lignin precursors*. Physicochemical Problems of Mineral Processing, 49, 463–473.
- KLAPISZEWSKI L., NOWACKA M., MILCZAREK G., JESIONOWSKI T., 2013b, *Physicochemical and electrokinetic properties of silica/lignin biocomposites*. Carbohydrate Polymers, 94, 345–355.
- KLAPISZEWSKI L., ZDARTA J., SZATKOWSKI T., WYSOKOWSKI M., NOWACKA M., SZWARC-RZEPKA K., BARTCZAK P., SIWIŃSKA-STAFIŃSKA K., EHRlich H., JESIONOWSKI T., 2014, *Silica/lignosulfonate hybrid materials: Preparation and characterization*. Central European Journal of Chemistry, 12, 719–735.
- KLAPISZEWSKI L., BARTCZAK P., WYSOKOWSKI M., JANKOWSKA M., KABAT K., JESIONOWSKI T., 2015, *Silica conjugated with kraft lignin and its use as a novel 'green' sorbent for hazardous metal ions removal*. Chemical Engineering Journal, 260, 684–693.
- KRYSZTAFKIEWICZ A., RAGER B., JESIONOWSKI T., 1997, *The effect of surface modification on physicochemical properties of precipitated silica*. Journal of Materials Science, 32, 1333–1339.
- LANGHE H., DECINA S., CRESTINI C., 2013, *Oxidative upgrade of lignin – Recent routes reviewed*. European Polymer Journal, 49, 1151–1173.
- LOTA G., MILCZAREK G., 2011, *The effect of lignosulfonates as electrolyte additives on the electrochemical performance of supercapacitors*. Electrochemistry Communications, 13, 470–473.
- MEISTER J.J., 2002, *Modification of lignin*. Journal of Macromolecular Science C: Polymer Reviews, 42, 235–289.
- MISHRA S.B., MISHRA A.K., KRAUSE R.W., MAMBA B.B., 2009, *Synthesis of silicon carbide nanowires from a hybrid of amorphous biopolymer and sol-gel derived silica*. Journal of the American Ceramic Society, 92, 3052–3058.
- RALPH J., LUNDQUIST K., BRUNOW G., LU F., KIM H., SCHATZ P.F., MARITA J.M., HATFIELD R.D., RALPH S.A., CHRISTENSEN J.H., BOERJAN W., 2004, *Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenylpropanoids*. Phytochemistry Reviews, 3, 29–60.
- ROY S., DIXIT C.K., WOOLLEY R., McCRAITH B.D., O'KENNEDY R., McDONAGH C., 2010, *Novel multiparametric approach to elucidate the surface amine-silanization reaction profile on fluorescent silica nanoparticles*. Langmuir, 26, 18125–18134.
- STÖBER W., FINK A., BOHN E., 1968, *Controlled growth of monodisperse silica spheres in the micron size range*. Journal of Colloid and Interface Science, 26, 62–69.
- SZWARC-RZEPKA K., CIESIELCZYK F., JESIONOWSKI T., 2013, *Preparation and physicochemical properties of functionalized silica/octamethacryl-silsesquioxane hybrid systems*. Journal of Nanomaterials, Article ID 674237, 1–15.
- TEJADO A., PENA C., LABIDI J., ECHEVERRIA J.M., MONDRAGON I., 2007, *Physico-chemical characterization of lignin from different sources for use in phenol-formaldehyde resin synthesis*. Bioresource Technology, 98, 1655–1663.
- TELYSHEVA G., DIZHBITE T., EVTUGUIN D., MIRONOVA-ULMANE N., LEBEDEVA G., ANDERSONE A., BIKOVENS O., CHIRKOVA J., BELKOVA L., 2009, *Design of siliceous lignins – novel organic/inorganic hybrid sorbent materials*. Scripta Materialia, 60, 687–690.
- TERTYKH V.A., YANISHPOLSKII V.V., BOL'BUKH Y., 2003, *Synthesis and characterization of functional chemically modified silica fillers*. Macromolecular Symposia, 194, 141–146.

- TERTYKH V.A., IVASHCHENKO N.A., YANISHPOLSKII V.V., KHAINAKOV S.A., 2013, *Platinum nanoparticles on the surface of silica modified with silicon hydride groups*. *Materials Science & Engineering Technology*, 44, 239–243.
- VANHOLME R., DEMEDTS B., MORREEL K., RALPH J., BOERJAN W., 2010, *Lignin biosynthesis and structure*. *Plant Physiology*, 153, 895–905.
- WYPYCH G., 2010, *Handbook of Fillers*, ChemTec Publishing, Toronto.
- ZAKZESKI J., JONGERIUS A.L., WECKHUYSEN B.M., 2010, *Transition metal catalysed oxidation of Alcell lignin, soda lignin, and lignin model compounds in ionic liquid*. *Green Chemistry*, 12, 1225–1236.
- ZAKZESKI J., BRUIJNINEX P.C.A., WECKHUYSEN B.M., 2011, *In situ spectroscopic investigation of the cobalt-catalyzed oxidation of lignin model compounds in ionic liquids*. *Green Chemistry*, 13, 671–680.
- ZURAWSKA J., KRYSZTAFKIEWICZ A., JESIONOWSKI T., 2003, *Active silicas obtained by precipitation from mixtures of sodium metasilicate and ammonium chloride solutions*. *Journal of Chemical Technology and Biotechnology*, 78, 534–541.